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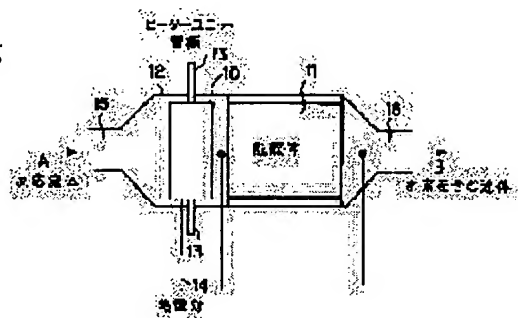
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(54) REFORMING REACTION DEVICE, CATALYTIC DEVICE, EXOTHERMIC CATALYTIC BODY USED FOR THE SAME AND OPERATION OF REFORMING REACTION DEVICE

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a reforming reaction device capable of generating a high purity hydrogen for a fuel cell as industrial or on-vehicle use for a short time, a catalytic device, an exothermic catalytic body used for the same and the operating method.

**SOLUTION:** The reforming reaction device is formed by arranging the catalytic body 11 for generating hydrogen from a reaction fluid A containing an organic compound or carbon monoxide by the catalytic reaction and a heater unit 10 capable of generating heat by supplying current in a fluid flow passage 12. The exothermic catalytic body is constituted so as to contain one of a sintered compact, a metallic body and the combined body, at least a part of which has exothermic resistive property, and a combined body of a heat resistant body and/or a metallic body, which has no exothermic resistive property itself, and the catalyst capable of generating hydrogen from the reaction fluid containing the organic compound or carbon monoxide, to have porosity, into which the reaction fluid is diffused, and to enable to generate heat by passing current.



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**CLAIMS**

[Claim(s)]

[Claim 1] A reforming reactor characterized by coming to arrange a catalyst object made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide, and a heater unit in which energization pyrexia is possible in fluid passage.

[Claim 2] A reforming reactor according to claim 1 with which this heater unit consists of a vesicular structure object.

[Claim 3] A reforming reactor according to claim 1 with which this heater unit consists of a honeycomb structure object.

[Claim 4] A reforming reactor given in any 1 term of claims 1-3 in which this catalyst object contains a catalyst which has a catalysis of a steam-reforming reaction, a partial oxidation reaction and one reaction of the decomposition reactions, CO water gas shift reaction, and/or CO selective oxidation catalytic reaction.

[Claim 5] A reforming reactor given in any 1 term of claims 1-4 which make it come to contain a catalyst which has a catalysis of a steam-reforming reaction, a partial oxidation reaction and one reaction of the decomposition reactions, CO water gas shift reaction, and/or CO selective oxidation catalytic reaction on this heater unit.

[Claim 6] An exoergic resistive characteristic is a reforming reactor given in any 1 term of claims 1-5 which it comes to consist of either heat-resistant material, said sintered compact and/or complex with said metal \*\*\*\* although there is nothing a sintered compact with which this heater unit has an exoergic resistive characteristic, metal \*\*\*\*, these complex, or in itself.

[Claim 7] A reforming reactor given in any 1 term of claims 1-6 which come to consist of these catalyst objects at least one or more honeycomb structure objects.

[Claim 8] A reforming reactor given in any 1 term of claims 1-7 which come to arrange this heater unit in the upstream of this catalyst object.

[Claim 9] A reforming reactor given in any 1 term of claims 1-7 which come to arrange this heater unit among two or more catalyst objects.

[Claim 10] a reforming reactor given in any 1 term of claims 1-7 which come to arrange this heater unit in a back-wash side of this catalyst object.

[Claim 11] a reforming reactor given in any 1 term of claims 1-10 which come to arrange a heat exchanger in a back-wash side of this catalyst object, or the middle of two or more catalyst objects.

[Claim 12] A reforming reactor given in any 1 term of claims 1-11 which heat this catalyst object and/or this fluid with heat collected by this heat exchanger.

[Claim 13] A reforming reactor characterized by being the reforming reactor which comes to arrange a catalyst object made to generate hydrogen in fluid passage, and these some catalyst objects [ at least ] being constituted from a reaction fluid containing an organic compound or a carbon monoxide by catalytic reaction possible [ pyrexia ] by energization.

[Claim 14] A reforming reactor according to claim 13 with which this catalyst object consists of a vesicular structure object.

[Claim 15] A reforming reactor according to claim 13 with which this catalyst object consists of a honeycomb structure object.

[Claim 16] A reforming reactor given in any 1 term of claims 13-15 in which this catalyst object contains a catalyst which has a catalysis of a steam-reforming reaction, a partial oxidation reaction and one reaction of the decomposition reactions, CO water gas shift reaction, and/or CO selective oxidation catalytic reaction.

[Claim 17] An exoergic resistive characteristic is a reforming reactor given in any 1 term of claims 13-16 containing a catalyst which has a catalysis of a reaction of either [ either heat-resistant material, said sintered compact and/or complex with said metal \*\*\*\* and ] a steam-reforming reaction, a partial oxidation reaction and a decomposition reaction, CO water gas shift reaction, and/or CO selective oxidation catalytic reaction although there is nothing a

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sintered compact with which this catalyst object has an exoergic resistive characteristic, metal \*\*\*\*, these complex, or in itself.

[Claim 18] A reforming reactor given in any 1 term of claims 13-17 which come to consist of these catalyst objects at least one or more honeycomb structure objects.

[Claim 19] A reforming reactor given in any 1 term of claims 13-18 from which an upstream portion is constituted by energization possible [ pyrexia ] at least in fluid passage of this catalyst object.

[Claim 20] a reforming reactor given in any 1 term of claims 13-19 which come to arrange a heat exchanger in a back-wash side of this catalyst object, or the middle of two or more catalyst objects.

[Claim 21] A reforming reactor given in any 1 term of claims 13-20 which heat a catalyst object and/or a reaction fluid with heat collected by this heat exchanger.

[Claim 22] Catalyst equipment characterized by coming to arrange a heater unit in which energization pyrexia is possible, and a catalyst object which causes endothermic reaction in fluid passage.

[Claim 23] Catalyst equipment characterized by coming to arrange a catalyst object containing a catalyst which some catalyst objects [ at least ] are constituted by energization possible [ pyrexia ], and causes endothermic reaction in fluid passage.

[Claim 24] they be the pyrexia and the catalyst object characterize by to be constitute by energization possible [ pyrexia ] while it have the porosity which a catalyst which generate hydrogen by catalytic reaction be contain [ porosity ] from a reaction fluid containing either , and an organic compound or a carbon monoxide of heat-resistant material , said sintered compact , and/or complex with said metal \*\*\*\* , and make a reaction fluid diffuse , although there be no exoergic resistive characteristic the sintered compact in which at least a part have an exoergic resistive characteristic by energization , metal \*\*\*\* , these complex , or in itself .

[Claim 25] Pyrexia and a catalyst object according to claim 24 with which this pyrexia and catalyst object consist of a vesicular structure object.

[Claim 26] Pyrexia and a catalyst object according to claim 24 or 25 with which this pyrexia and catalyst object consist of a honeycomb structure object.

[Claim 27] Pyrexia and a catalyst object given in any 1 term of claims 24-26 which carried out covering support of the catalyst which generates hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide on a honeycomb structure object of quality of a metal which shows a heat generation characteristic.

[Claim 28] Pyrexia and a catalyst object given in any 1 term of claims 24-27 to which a honeycomb structure object of this quality of a metal uses an alloy of Fe-Cr-aluminum, Fe-Cr, Fe-aluminum, nickel-Cr, and nickel-aluminum as a principal component.

[Claim 29] Pyrexia and a catalyst object given in any 1 term of claims 24-28 which contain at least one sort in a metallic element to which a catalyst which generates hydrogen belongs to a VB-VIII group, IB group, and an IIB group in the periodic table of a long period by catalytic reaction from a reaction fluid containing this organic compound or a carbon monoxide, and a heat-resistant oxide as a principal component.

[Claim 30] Pyrexia and a catalyst object according to claim 29 said whose metallic element is at least one sort in a metallic element of a VIII group's metallic element, V, Cr, Mo, W and Re, and IB group, and a metallic element of Zn.

[Claim 31] Pyrexia and a catalyst object according to claim 29 said whose heat-resistant oxides are aluminum  $2O_3$ ,  $SiO_2$ ,  $TiO_2$ ,  $ZrO_2$  and  $MgO$  or a zeolite, SAPO, ALPO, stratified compounds, and these multiple oxides.

[Claim 32] Pyrexia and a catalyst object given in any 1 term of claims 24-31 whose hole density a hole equivalent diameter of this pyrexia and catalyst object is 0.5-10mm, and is 50 - 95%.

[Claim 33] An exoergic resistive characteristic is pyrexia and a catalyst object characterized by being constituted by energization possible [ pyrexia ] while having porosity which either heat-resistant material, said sintered compact and/or complex with said metal \*\*\*\* and a catalyst that causes endothermic reaction are contained [ porosity ], and makes a reaction fluid diffuse, although there is nothing a sintered compact in which at least a part has an exoergic resistive characteristic by energization, metal \*\*\*\*, these complex, or in itself.

[Claim 34] An operating method of a reforming reactor characterized by making this heater unit generate heat by energization, and making hydrogen generate in an operating method of a reforming reactor which comes to arrange a catalyst object made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide, and a heater unit in which energization pyrexia is possible in fluid passage at the time of \*\*\*\* starting of this reactor.

[Claim 35] An operating method of a reforming reactor with which a catalyst object made to generate hydrogen by a reaction fluid containing an organic compound or a carbon monoxide to catalytic reaction is arranged in fluid passage, and these some catalyst objects [ at least ] are characterized by making this catalyst object generate heat by energization

at the time of \*\*\*\* starting of this reactor, and making hydrogen generate in an operating method of a reforming reactor constituted possible [ pyrexia ] by energization.

[Claim 36] An operating method of a reforming reactor characterized by making this heater unit generate heat by energization, and generating hydrogen so that catalytic reaction may maintain reaction temperature of this catalyst object at homogeneity in an operating method of a reforming reactor which comes to arrange a catalyst object made to generate hydrogen and a heater unit in which energization pyrexia is possible in fluid passage from a reaction fluid containing an organic compound or a carbon monoxide.

[Claim 37] An operating method of a reforming reactor characterized by to arrange a catalyst object made to generate hydrogen by catalytic reaction in fluid passage from a reaction fluid containing an organic compound or a carbon monoxide, to make this catalyst object generate heat by energization so that these some catalyst objects [ at least ] may maintain reaction temperature of this catalyst object at homogeneity in an operating method of a reforming reactor constituted possible [ pyrexia ] by energization, and to generate hydrogen.

[Claim 38] a heater unit or a catalyst based on endothermic reaction which may occur by steam-reforming reaction or decomposition reaction -- an operating method of a reforming reactor according to claim 36 which makes this heater unit generate heat by energization, and generates hydrogen to a temperature fall of a catalyst in the living body.

[Claim 39] a heater unit or a catalyst based on endothermic reaction which may occur by steam-reforming reaction or decomposition reaction -- an operating method of a reforming reactor according to claim 37 which makes this catalyst object generate heat by energization, and generates hydrogen to a temperature fall of a catalyst in the living body.

[Claim 40] a heater unit or a catalyst based on endothermic reaction which may occur by steam-reforming reaction or decomposition reaction -- an operating method of a reforming reactor according to claim 38 which controls energization to a temperature fall of a catalyst in the living body so that temperature of this heater unit becomes homogeneity.

[Claim 41] a heater unit or a catalyst based on endothermic reaction which may occur by steam-reforming reaction or decomposition reaction -- an operating method of a reforming reactor according to claim 39 which controls energization to a temperature fall of a catalyst in the living body so that temperature of this catalyst object becomes homogeneity.

[Claim 42] An operating method of catalyst equipment characterized by making this heater unit generate heat by energization in an operating method of catalyst equipment which comes to arrange a heater unit in which energization pyrexia is possible, and a catalyst object which causes endothermic reaction in fluid passage.

[Claim 43] An operating method of catalyst equipment characterized by making this catalyst object generate heat by energization in an operating method of catalyst equipment which comes to arrange a catalyst object containing a catalyst which some catalyst objects [ at least ] are constituted by energization possible [ pyrexia ], and causes endothermic reaction in fluid passage.

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**DETAILED DESCRIPTION****[Detailed Description of the Invention]**

**[0001]**

**[The technical field to which invention belongs]** This invention relates to the operating method of the reforming reactor for hydrogen generating which can be suitably used as industrial use and an object for mount, catalyst equipment, the pyrexia and the catalyst object that are used for them, and a reforming reactor.

**[0002]**

**[Description of the Prior Art]** In recent years, clean-ization in electric manufacture attracts attention, and the interest about a fuel cell is increasing. Generating efficiency of a fuel cell is high, and its yield of a carbon dioxide (CO<sub>2</sub>) is also low, and it has the advantage which, in addition, suppresses generating of harmful gas, such as a carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>). Therefore, development for using a fuel cell for the electric organ and the object for mount of an on-site (On-site) mold recently is performed. In order to generate the electrical and electric equipment with a fuel cell, the hydrogen of a high grade is needed, and catalytic reaction generates hydrogen mainly by using alcohol, such as hydrocarbons, such as butane and a propane, and a methanol, CO, etc. as a start raw material.

**[0003]** Although the main reaction of hydrogen composition is a steam-reforming reaction (Steam Reforming) which occurs under existence of a steam and a catalyst, and it is dependent also on the material of a start raw material, since it is the point how a catalyst is heated to the temperature of the request to homogeneity, and caking will occur in it if reaction temperature falls in eye backlash which is generally endothermic reaction, and it leads to deactivation of a catalyst at it, as for this reaction, an industry top needs great concentration for layout of a reactor.

**[0004]** Moreover, although the above-mentioned steam-reforming reaction needed comparatively big catalyst volume to throughput since the reaction rate was not quick like the combustion reaction, the technical field as which the pre-heating of a catalyst takes time amount since the operative temperature of a catalyst is high, and generating of hydrogen is promptly required of a mold on site or mount had many problems.

**[0005]** In the conventional catalyst process, although the method of carrying out heat tracing of the catalyst was generally used, in the case of fixed-bed flow system, it is difficult to tell heat to a catalyst-bed center section, and the complicated reaction process which heats the reactor of a multipipe type with heating media, such as a metal bath and a combustion gas, was needed with the comparatively big coil.

**[0006]** Moreover, although the method of supplying a combustion gas (gaseous phase reaction and contact combustion) to the interior of a coil, and heating a catalyst by convective heat transfer as other conventional methods is used, since CO<sub>2</sub> occurs by combustion while bringing about the fall of labile, in order to make a fluid flow rate increase, it cannot be said to be a desirable method.

**[0007]** Moreover, in the generation gas obtained at the steam-reforming reaction, since it has a poisoning operation to Pt system electrode used for a fuel cell, CO which the purity of hydrogen generated like hydrogen highly [ in order to use for fuel cells ] raises the purity of hydrogen by CO water gas shift reaction (aquosity shift reaction) or alternative oxidation reaction of only CO. However, many technical technical problems occur about whether what we do into an operation condition with the pre-heating of these catalysts, and whether these reactions are advanced to stability.

**[0008]** As other reactions which generate hydrogen from a hydrocarbon etc., instead of a steam-reforming reaction, hydrogen and CO are generated and there is a method of obtaining hydrogen by the above-mentioned CO water gas shift reaction or CO alternative oxidation reaction by the partial oxidation reaction of a hydrocarbon. Although the 1st-step partial oxidation reaction is exothermic reaction and the problem about supply of heat is mitigated, generally reaction temperature is higher than a steam-reforming reaction, and there is no technology completed on the process about how the temperature of a catalyst is maintained too, and whether the hydrogen for the fuel cells of a high grade is generated a mold on site and for mount for a short period of time. Furthermore, a decomposition reaction is mentioned as a reaction

which generates hydrogen from a hydrocarbon etc. Although the decomposition reaction which generates hydrogen from a methanol specifically occurs, this reaction is endothermic reaction as well as a steam-reforming reaction, and has the same problem as the above.

[0009] Also in the industry which needs hydrogen in large quantities, for example, an ammonia synthesis reaction and a hydrogenation reaction, hydrogenation desulfurization, etc., reaction effectiveness is raised, it can operate by low energy, and starting of a reactor is shortened, and it can be said that there is room of amelioration plentifully in the point which does not discharge a unconverted gas.

[0010]

[Problem(s) to be Solved by the Invention] Therefore, the place which this invention is made in view of the technical problem of the above-mentioned conventional technology, and is made into the purpose is to offer the operating method of the reforming reactor which can generate the hydrogen for the fuel cells of a high grade in a short time, catalyst equipment, the pyrexia and the catalyst object which are used for them, and a reforming reactor as industrial use or an object for mount.

[Means for Solving the Problem] According to this invention, a reforming reactor (1st invention) characterized by coming to arrange a catalyst object made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide and a heater unit in which energization pyrexia is possible in fluid passage is offered. Moreover, according to this invention, a reforming reactor (2nd invention) characterized by being the reforming reactor which comes to arrange a catalyst object made to generate hydrogen in fluid passage, and these some catalyst objects [ at least ] being constituted from a reaction fluid containing an organic compound or a carbon monoxide by catalytic reaction possible [ pyrexia ] by energization is offered.

[0012] A sintered compact in which at least a part furthermore has an exoergic resistive characteristic by energization according to this invention, metal \*\*\*\*, or these complex, Although there is no exoergic resistive characteristic in itself, either [ or ] heat-resistant material, said sintered compact and/or complex with said metal \*\*\*\*. A catalyst which generates hydrogen by catalytic reaction is contained from a reaction fluid containing an organic compound or a carbon monoxide, and while having porosity which makes a reaction fluid diffuse, pyrexia and a catalyst object (3rd invention) characterized by being constituted by energization possible [ pyrexia ] are offered.

[0013] A catalyst object which is made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide further again according to this invention, In an operating method of a reforming reactor which comes to arrange a heater unit in which energization pyrexia is possible in fluid passage An operating method of a reforming reactor characterized by making this heater unit generate heat by energization, and making hydrogen generate at the time of \*\*\*\* starting of this reactor (4th invention), And a catalyst object made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide is arranged in fluid passage. An operating method (5th invention) of a reforming reactor characterized by for these some catalyst objects [ at least ] making this catalyst object generate heat by energization, and making hydrogen generate in an operating method of a reforming reactor constituted by energization possible [ pyrexia ] at the time of \*\*\*\* starting of this reactor is offered.

[0014] Furthermore, according to this invention, a catalyst object made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide and a heater unit in which energization pyrexia is possible are set to an operating method of a reforming reactor which it comes to arrange in fluid passage. An operating method of a reforming reactor characterized by making this heater unit generate heat by energization, and generating hydrogen so that reaction temperature of this catalyst object may be maintained at homogeneity (6th invention), And a catalyst object made to generate hydrogen by catalytic reaction from a reaction fluid containing an organic compound or a carbon monoxide is arranged in fluid passage. In an operating method of a reforming reactor with which these some catalyst objects [ at least ] are constituted by energization possible [ pyrexia ] An operating method (7th invention) of a reforming reactor characterized by making this catalyst object generate heat by energization, and generating hydrogen so that reaction temperature of this catalyst object may be maintained at homogeneity is offered.

[0015] According to this invention, further again A heater unit in which energization pyrexia is possible, Catalyst equipment characterized by coming to arrange a catalyst object which causes endothermic reaction in fluid passage (8th invention), And catalyst equipment (9th invention) characterized by coming to arrange a catalyst object containing a catalyst which some catalyst objects [ at least ] are constituted by energization possible [ pyrexia ], and causes endothermic reaction in fluid passage is offered. Moreover, a sintered compact in which at least a part has an exoergic resistive characteristic by energization according to this invention, metal \*\*\*\*, or these complex, Although there is no exoergic resistive characteristic in itself, either [ or ] heat-resistant material, said sintered compact and/or complex with



said metal \*\*\*\*. A catalyst which causes endothermic reaction is contained, and while having porosity which makes a reaction fluid diffuse, pyrexia and a catalyst object (10th invention) characterized by being constituted by energization possible [ pyrexia ] are offered. Furthermore, according to this invention, a heater unit in which energization pyrexia is possible, and a catalyst object which causes endothermic reaction are set to an operating method of catalyst equipment which it comes to arrange in fluid passage. An operating method of catalyst equipment characterized by making this heater unit generate heat by energization (11th invention), And a catalyst object containing a catalyst which some catalyst objects [ at least ] are constituted by energization possible [ pyrexia ], and causes endothermic reaction is set to an operating method of catalyst equipment which it comes to arrange in fluid passage. An operating method (12th invention) of catalyst equipment characterized by making this catalyst object generate heat by energization is offered. [0016]

[Embodiment of the Invention] According to this invention, optimum dose generating of the hydrogen of a high grade can be made to be able to carry out for a short period of time, and it can apply to it preferably as a mold on site or a hydrogen generator for mount. Hereafter, although the gestalt of operation of this invention is explained, this invention is not limited to the gestalt of these operations.

[0017] In this invention, the reaction fluid which contains the organic compound or carbon monoxide (CO) which consists of alcohol, such as hydrocarbons, such as butane and a propane, and a methanol, as a start raw material for obtaining hydrogen is used. From a viewpoint of transportation of a bomb or a pipeline, although an alcoholic raw material like a gasoline or a methanol which can be carried with a liquid is desirable when a hydrocarbon considers the handling for mount preferably, it is not limited to these at all. CO is also poisonous gas and is not desirable as a start component.

[0018] The main reaction in the reforming reactor of this invention is a steam-reforming reaction which occurs under steam existence, and since CO of a by-product carries out poisoning of the electrode of a fuel cell in order to obtain H<sub>2</sub> of a high grade further, it reduces CO by CO water gas shift reaction or CO partial oxidation reaction. The example of a reaction using butane is shown below.

(1)  $C_4H_{10} + 9H_2O \rightarrow 9H_2 + 4CO$  Steam-reforming reaction (2)  $CO + H_2O \rightarrow CO_2 + H_2$  CO water gas shift reaction (3)

$CO + \frac{1}{2}O_2 \rightarrow CO_2$  CO alternative oxidation reaction [0019] As another reaction which obtains hydrogen, there is also the technique of using a partial oxidation reaction instead of a steam-reforming reaction.

(4)  $C_4H_{10} + 2O_2 \rightarrow 4CO + 5H_2$  Partial oxidation reaction [0020] Following on a partial oxidation reaction, the reaction of the above (2) and (3) is usually advanced, and the purity of hydrogen is raised. Although the method of acquiring the method of obtaining hydrogen from a reaction (1) for hydrogen from a steam reforming process and a reaction (4) is called a partial oxidation method, this invention is applicable to any method. Although it is arbitrary about whether a steam reforming process is used or a partial oxidation method is used, for mount, the steam reforming process attracts attention by the partial oxidation method about alcohol, such as a methanol, in the gasoline. Generally, it is easy to obtain the hydrogen of a high grade at low temperature, and the steam reforming process is more efficient.

[0021] Moreover, there are the following two kinds as a reaction which generates hydrogen from a methanol.

(5)  $CH_3OH \rightarrow CO + H_2$  Decomposition reaction (endothermic)

(6)  $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$  Steam-reforming reaction (endothermic)

[0022] Although the catalyst used for these reactions is mentioned later, a usually different catalyst is used and reaction temperature also differs. Generally the reaction of (1), (5), and (6) is endothermic reaction, and needs the temperature of 500 degrees C or more. (2) or (3) reaction -- exothermic reaction -- it is -- 300 degrees C or less -- it is made to go on at low temperature comparatively The reaction of (4) is exothermic reaction and needs the reaction temperature of 500 degrees C or more too. in order to obtain the hydrogen of a high grade -- usually -- the above -- each catalyst is arranged for the reaction of (1 [(5), (6)]), (2), (3) or (4), (2), and (3) to a serial in fluid passage. [ or ] In addition, you may be a reforming reactor by (1 [(5), (6)] or the reaction of (4), and when using CO as a start raw material, (3) is made to react in the hydrogen concentration to need (2) or if needed. [ or ]

[0023] Hereafter, the operating method of the reforming reactor concerning this invention, catalyst equipment, the pyrexia and the catalyst object that are used for them, and a reforming reactor is explained in detail. This application the 1st invention relates to the reforming reactor which comes to arrange the catalyst object made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide, and the heater unit which can be energized in fluid passage. One embodiment of this reforming reactor is shown in drawing 1.

[0024] In drawing 1, the heater unit 10 and the catalyst object 11 are arranged in the can (fluid passage) 12 of the quality of a metal, and constitute a reforming reactor. The heater unit 10 has an electrode 13 and the electrical and electric equipment is switched on from the external power which is not illustrated. Usually, the heater unit 10 is arranged at the upstream of the catalyst object 11. the sensor 14 for heater unit 10 control (a thermocouple etc. is

included) is arranged at the back-wash side of the heater unit 10 or the heater unit 10. The reaction fluid A flows from an inlet port 15, and results in the outlet hole 16 through the heater unit 10 and the catalyst object 11. the fluid B containing the obtained hydrogen is conveyed to the fuel cell section arranged to the back-wash side of a reforming reactor.

[0025] although the cylinder which consists of a Nichrome presentation, and a tabular thing may be arranged all over fluid passage, in order to heat efficiently the catalyst object 11 arranged, for example to a back-wash side, the thing of a porosity object, for example, the shape of cavernous tissue of 50% or more of hole density, a blanket-like thing, a filter-like thing, and the thing of the configuration of a honeycomb structure object (a tabular catalyst is also included) can apply the heater unit 10 suitably. Since especially the honeycomb structure object that has a linear through tube in the flow direction of the reaction fluid A has small heat-conducting characteristic and pressure loss which are done to a reaction fluid, it is the most desirable.

[0026] The catalyst object 11 contains at least either of the catalyst components which has a catalysis about the above-mentioned steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, CO alternative oxidation reaction, etc. Among these, although CO alternative oxidation reaction is the purpose which reduces CO and it is not related to direct hydrogen composition, when you need high hydrogen concentration, it is important, and in order to incorporate in a reforming reactor, it includes in the catalyst object 11 in this invention.

[0027] Although the heating element itself is sufficient as the heater unit 10, it is more more desirable to contain either of the catalysts which has catalyses, such as a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO partial oxidation reaction, from the pre-heating property at the time of \*\*\*\* starting of the catalyst object 11 or a viewpoint of promotion of a reaction and temperature equalization of the catalyst object 11 at the time of steady operation. Although there is also a method of making a catalyst and a heating element intermingled as a method of making a catalyst containing, the method of carrying out covering support of the catalyst on the surface of a heating element can be used preferably. The heater unit which covered the catalyst on the honeycomb structure object which has a heat generation characteristic further on the spongy porosity object in which the above-mentioned heat generation characteristic is shown from a viewpoint which can expect labile is the most desirable.

[0028] the sintered compact in which a heat generation characteristic is shown as a material of the heater unit 10, i.e., barium titanate, (material called a common name PTC and positive-like resistive characteristic), the carbide of SiC and MoSi<sub>2</sub> grade, the superconduction oxide of Y and Bi system, the oxygen ion conductor of perovskite or ZrO<sub>2</sub> grade in which the negative-like resistive characteristic is shown, other silicide, and a bora -- from the id, night RAIDO, and the concept of a sintered compact, although it shifts, ion conductivity glass can be used. Furthermore, as metal \*\*\*\* which shows an exoergic resistive characteristic, although it does not have an exoergic resistive characteristic these metals and in itself [ the alloy presentation of the ferrite presentation of Fe-Cr-aluminum, nickel-Cr Fe-aluminum, Fe-Cr nickel-aluminum, etc., and ], the cermet which is heat-resistant material and which compounded the alumina etc. can be used.

[0029] The material used for the above-mentioned heater unit is independent respectively, or it may be used, making it compound-ize. Moreover, compound-izing with a catalyst component is also possible. An important thing is that the property which generates heat by energization is shown, and it is not limited in material. From the point of cost and manufacturability, the alloy presentation of Fe-Cr-aluminum, Fe-aluminum, Fe-Cr, etc. is desirable. These are already put in practical use as a catalytic converter for automobiles, and it excels also in thermal resistance and thermal shock resistance, and they have easily the advantage which can be created on a honeycomb structure object by the rolling method or the powder metallurgy method. As an example of the heater of a honeycomb structure object, what is shown in JP,3-295184,A ( drawing 2 ), and the thing ( drawing 3 ) shown in a \*\*\*\*\* No. 500911 [ three to ] official report are mentioned.

[0030] The electrode 13 for energizing to the heater unit 10 is connected to the heater unit 10, and the electrical and electric equipment is supplied to it from an external power. It is possible to use the power supply of a battery, an AC dynamo, a capacitor (capacitor), etc., etc. in for mount. The heater unit 10 needs to adjust resistance according to injection power, voltage, etc. Although these adjustment methods are not limited, when the heater unit 10 is a honeycomb structure object, as shown in JP,3-295184,A and a \*\*\*\*\* No. 500911 [ three to ] official report, resistance can be adjusted by forming a slit and a gap.

[0031] The catalyst object 11 is used as a bead, a pellet, the shape of the shape of a grain, or a honeycomb, and a tabular configuration. Although a bead etc. is preferably used in respect of fluid mixing or heat conduction , since the reaction fluid in fluid passage is heated suitably and convective heat transfer is spread by heat mainly to the catalyst object 11 by combining with the heater unit 10 of this invention , it is desirable from the point of a pressure loss or a mechanical strength to use the honeycomb structure object which consists of the shape of a honeycomb or a tabular configuration .



A honeycomb structure object means the structure which has the through tube (cel) substantially surrounded by the uniform septum, and also includes a tabular catalyst.

[0032] When using the catalyst object 11 as a configuration of a honeycomb structure object, covering support may be carried out and a catalyst component may be used for the honeycomb support which may honeycomb-size catalyst component itself and consists of inactive materials, such as cordierite and a mullite.

[0033] The catalyst object 11 usually arranges the catalyst of anti-application [ oxidation / steam-reforming reaction, partial oxidation reaction and one reaction / of the decomposition reactions /, CO water gas shift reaction, and CO alternative ] to a serial. In the case of a honeycomb structure object, what classified each catalyst into one honeycomb structure object is sufficient as the catalyst object 11, but since reaction temperature differs, respectively, it is desirable to arrange two or more catalyst objects in a reforming reactor. It is because this gentleman can arrange arrangement of the heat exchanger for heat recovery, the introductory hole of auxiliary oxygen required for CO alternative oxidation reaction, etc.

[0034] As an array over the catalyst object 11 of the heater unit 10, as shown in drawing 4, it is desirable to arrange for the maximum upstream of two or more catalyst objects 11 (catalyst object 11a [ 1st ], catalyst object 11b [ 2nd ], 3rd catalyst object 11c). Thereby, the pre-heating property of the catalyst object 11 whole improves. As another embodiment, as shown in drawing 5, it is also possible to install heater unit 10b between [ other than heater unit 10a which divides the catalyst object 11 into plurality and is arranged for the maximum upstream ] 1st catalyst object 11a and 2nd catalyst object 11b. In this case, heater unit 10b will have the function which maintains an improvement of the pre-heating property of 2nd catalyst object 11b, and the temperature of 2nd catalyst object 11b at homogeneity. Moreover, it is also possible like drawing 6 to install the heater units 10b and 10c, respectively between 1st catalyst object 11a and 2nd catalyst object 11b and between 2nd catalyst object 11b and 3rd catalyst object 11c. Furthermore, as another embodiment, as shown in drawing 7, it is also possible to arrange heater unit 10c to the last style side. in this case, it is because it may be necessary to arrange the further catalyst object 11 to the back-wash side of that heater unit 10c if it is heater unit 10c which comes to support CO alternative oxidation catalyst. If the heater unit 10 contains the catalyst for a steam-reforming reaction or a partial oxidation reaction, CO water gas shift reaction, and CO partial oxidation reaction arbitrarily as for in [ how many ] the array sequence of the heater unit 10 and the catalyst object 11, and a reforming reactor it arranges like the above, combination like the heater unit 10, the catalyst object 11, and the heater unit 10 is also free.

[0035] The ranges of the typical reaction temperature for a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO partial oxidation reaction are 500 degrees C or more, 200-300 degrees C, and 100-200 degrees C, respectively. Therefore, catalyst object of a steam-reforming reaction, a partial oxidation reaction, or a decomposition reaction Between the catalyst objects of CO water gas shift reaction, since a temperature gradient arises, as shown in drawing 8 - drawing 9, it is desirable to arrange and carry out heat recovery of the heat exchanger 17 into fluid passage. The collected heat heats the reaction fluid A, or uses it for heating of the catalyst object 11.

[0036] The embodiment of drawing 8 is an example which has arranged the heat exchanger 17 between 1st catalyst object 11a and 2nd catalyst object 11b, and after heat exchange of the reaction fluid A is carried out by the heat exchanger 17 and it is heated with a carburetor 18, it is introduced in a can 12. In addition, it is also possible to carry out heat exchange of the reaction fluid A after heating with a carburetor. Here, although the class of heat exchanger 17 is not limited, a juxtaductal type heat exchanger, a tabular mold heat exchanger, etc. can be used. Although the embodiment of drawing 9 as well as drawing 8 is the example which has arranged the heat exchanger 17 between 1st catalyst object 11a and 2nd catalyst object 11b, as a fluid by which heat exchange is carried out, it may not be limited to a reaction fluid but it may be a heating medium. Although passing in the direction which needs the heat of the upstream is generally desirable as for the fluid after heat exchange, it may be poured to the downstream.

[0037] Next, this application the 2nd invention is explained. The catalyst object 20 made to generate hydrogen from the reaction fluid with which this application the 2nd invention contains an organic compound or a carbon monoxide is arranged in fluid passage, and some catalyst objects [ at least ] 20 are related with the reforming reactor constituted by energization possible [ pyrexia ]. The embodiment of this reforming reactor is shown in drawing 10 and drawing 11.

[0038] The catalyst object 20 is arranged in the can 21 of the quality of a metal, has the electrode 22 for energization in catalyst object 20 the very thing, and consists of a configuration that a part or the whole of the catalyst object 20 generates heat, by energization. In addition, drawing 10 is the configuration that the whole catalyst object 20 generates heat by energization, and drawing 11 shows the configuration in which some catalyst objects 20 generate heat by energization. Therefore, this application the 2nd invention has the function in which catalyst object 20 itself generates heat by energization, to the heater unit 10 and the catalyst object 11 being separately arranged in a can 12, as for the

above-mentioned this application 1st invention, and an essential effect is made the same. In addition, the external power, the configuration of the sensor for temperature control and fluid passage, etc. are the same as the 1st invention.

[0039] Although it is the same as the heater unit 10 of the 1st invention, since the configuration of the catalyst object 20 in the 2nd invention is held and energized in a can 21, its porosity object of 50% or more of hole density is desirable, and it is the most desirable from the point of a heat-conducting characteristic or a pressure loss. [ of the thing of a honeycomb structure object ] Moreover, as shown in drawing 12 , the catalyst object 20 is put by making into a core material 23 for example, metal \*\*\*\* of the shape of the punching plate which consists of a material in which energization pyrexia is possible, or a mesh, and, finally the structure which it comes to finish setting up to a honeycomb or a tabular module is also contained in the honeycomb structure object of this application.

[0040] Although it is most desirable to use as a porous base the material in which the same pyrexia as the heater unit 10 of the 1st invention is possible, and to carry out covering support of the catalyst for a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO partial oxidation reaction on a base when using the porous catalyst object 20, it is not limited to this as well as the 1st invention.

[0041] Using as a base the honeycomb structure object which consists of an alloy presentation of Fe-Cr-aluminum, Fe-aluminum, Fe-Cr, etc. from the point of cost and manufacturability as most desirable example of the catalyst object 20, and carrying out covering support of the desired catalyst on this base is mentioned. In this case, it depends on the resistance adjusting method [ how the whole is generated heat partially ] in a catalyst object slack honeycomb structure object.

[0042] One suitable embodiment is shown below at drawing 13 . Two or more slits 26 are formed near [ fluid entrance 25 ] the catalyst object 20 which consists of a honeycomb structure object, and a kind of current circuit is formed. one slit 27 is formed in the back-wash portion of the catalyst object 20 which consists of a honeycomb structure object in the direction of the slit 26 of the fluid entrance 25, and the mode which goes direct. By installing in a fluid entrance 25 close-attendants side, an electrode 28 serves as the structure where form the zigzag pass of current along with the about 25 fluid entrance slit 26 in this way, consequently only a fluid entrance 25 close-attendants side generates heat. Thus, a heat generation characteristic is controllable to a request by preparing a slit and a gap to make the catalyst object 20 partial pyrexia.

[0043] The technique as the above-mentioned in which the technique of making the whole catalyst object 20 generate heat is also the same can be used. Furthermore, by arranging two or more catalyst objects 20 which can generate heat by energization in fluid passage as a reforming reactor by this application the 2nd invention, and changing resistance of each catalyst object Adjust or so that the whole catalyst object may become a uniform temperature A steam-reforming reaction, For every partial oxidation reaction or decomposition reaction, CO water gas shift reaction, and CO alternative oxidation anti-application The catalyst object which can be energized according to an individual is made to form, it can control by energization or the generating effectiveness of the hydrogen made into the purpose can be raised by the energization method (time amount, power, timing adjustment) of a catalyst object in which further two or more energization is possible so that it may become a desired temperature. In addition, this technique is applicable also in the heater unit in the 1st invention.

[0044] Even when it compares with the 1st invention and two or more catalyst objects which can be energized are used in the 2nd invention, as for each, it is desirable that it is really an object. In addition, with this point Although heat conduction is also multiplied and it is easy to acquire high thermal-conversion effectiveness and uniform temperature distribution, it is desirable for it not to be necessary to heat the mass whole catalyst object superfluously, and to compound the 1st invention and invention of the 2nd in to use partial pyrexia \*\*\*\* if needed. In addition, as shown in drawing 14 , when arranging the catalyst object 20 in which two or more energization is possible in a reforming reactor, energization control of each catalyst objects 20a, 20b, and 20c may be carried out independently, respectively, and it may connect with a serial or you may connect with connection and a pan with such combination at juxtaposition.

[0045] It is more desirable to heat the upstream, in order to raise the pre-heating nature of a catalyst object although the upstream, the downstream, and a core may be made to generate heat when making the catalyst object which can be energized generate heat partially. Moreover, how to attach distribution to radial is also considered. In the catalyst object of a steam-reforming reaction, in order that the core where the rate of flow of a reaction fluid is the quickest may bring about a bigger temperature fall by the reaction, a catalyst object with which a core generates heat from the periphery section is more desirable. This can say the same thing in the 1st invention also in the heater unit 10 arranged in the upstream (front) of the catalyst object 11 of a steam-reforming reaction, as shown in drawing 15 .

[0046] Also in the 2nd invention, since the reaction temperature of a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO alternative oxidation reaction differs It is desirable to arrange two or more catalyst objects in a reforming reactor. A heat exchanger A steam-reforming reaction,

it installs in the back-wash side of the catalyst object for a partial oxidation reaction or decomposition reactions, and heat recovery can be carried out and, ahead [ of CO alternative oxidation reaction / catalyst object ], an oxygen installation hole (installation of air is possible in practice) can be installed in heating a reaction fluid and a catalyst object \*\*\*\* if needed.

[0047] In the above, although the reforming reactor concerning this application the 1st and 2nd invention has been explained, the catalyst equipment which caught the above-mentioned invention from another viewpoint is explained below. That is, it is catalyst equipment (9th invention) which has arranged the catalyst object containing the catalyst which the catalyst equipment (8th invention) which has arranged the heater unit in which energization pyrexia is possible, and the catalyst object which causes endothermic reaction in fluid passage, and some catalyst objects [ at least ] are constituted by energization possible [ pyrexia ], and causes endothermic reaction in fluid passage. Thus, 8th and 9th invention is characterized by the point using the catalyst object as a means to give heat which at least a heater unit or a part can energization generate heat to the catalyst equipment which causes endothermic reaction, and the configuration of a heater unit and a catalyst object, a presentation, the quality of the material, and its array are the same as that of the 1st and 2nd above-mentioned invention. In addition, as an example of endothermic reaction, dehydrogenation besides a steam-reforming reaction which was described above, and a decomposition reaction can be mentioned.

[0048] Next, the pyrexia and the catalyst object in this application the 3rd invention are stated to details. In the 1st invention, although the material in which the heat generation characteristic used as a heater unit 10 is shown was stated to details, also in the 3rd invention, the same material is completely used as pyrogen. 3rd invention is characterized by having the porosity which the catalyst which generates hydrogen is contained [ porosity ] in this and makes it diffuse a reaction fluid. That is, although the pyrexia and the catalyst object in the 3rd invention consist of a vesicular structure, 50 - 95% of range of hole density is desirable. If hole density brings about increase of pressure loss at less than 50% and hole density exceeds 95%, the fall of a porosity object on the strength will be brought about.

[0049] The honeycomb structure object which has linear hole density to a reaction fluid in the porosity object in pyrexia and a catalyst object is one of the desirable embodiments. A honeycomb structure object is formed with the gestalt containing the catalyst which generates exoergic resistive-characteristic material and hydrogen. Although it is as the term of the heater unit of the 1st invention having described in what kind of form pyrogen is included, it is most desirable to use the quality of a metal with a high heat-conduction property. The ferrite system metal in this case has highly desirable thermal resistance. For example, it is a Fe-Cr-aluminum system and, in the content of Cr, aluminum content can use 3 - 15% of the weight of a thing ten to 40% of the weight. Furthermore, it is desirable to add a small amount of additives, such as a lanthanum system element, and Si, Y, and to raise metale thermal resistance. It is desirable to carry out covering support of the catalyst which generates hydrogen on the base of the honeycomb structure which consists of such quality of a metal.

[0050] Here, whether it is porosity or the base of honeycomb structure itself is nonvesicular like rolling foil metal, it is not cared about. Although reaction temperature is 900 degrees C or less, and exfoliation by the differential thermal expansion with the catalyst material which the heat capacity of the base itself is [ to use a porous base ] smaller, and was covered on the base can be prevented when a thermal shock is not so large, either, it is fully usable also nonvesicular. As porosity of a base, 5 - 40% is desirable.

[0051] Moreover, an insulating material and a gap are made for the rolling (punching metal) foil which the hole opened as a desirable operation gestalt to intervene by rolling up from another viewpoint, the base in which a heat generation characteristic is shown is created, and the example which carries out covering support of the catalyst which generates hydrogen further is given. A reaction fluid diffuses also in radial the through tube of a fluid flow direction and the honeycomb structure object opened in parallel via the through tube in the foil while flowing. In this way, it is considered from radial heat transfer of a honeycomb structure object being performed that the catalyst of endothermic reaction is effective in equalization of temperature distribution especially like a steam-reforming reaction. Such a honeycomb structure object has a remarkable operation also in the usual honeycomb structure object which is not energized.

[0052] The hole equivalent diameter of the honeycomb structure object which constitutes pyrexia and a catalyst object has the desirable range of 0.5-10mm. this hole -- the case where an equivalent diameter is less than 0.5mm -- the rise of a pressure loss -- bringing -- on the other hand -- a hole -- the fall of labile will be brought about if an equivalent diameter exceeds 10mm. As the number of cels of a honeycomb structure object, the range of 4-1500 cel / square inch is desirable, and it specifically decides suitably from a viewpoint of a pressure loss and labile.

[0053] As a catalyst which generates hydrogen from the reaction fluid containing an organic compound or a carbon monoxide, the component shown below can be used suitably. That is, at least one sort in the metallic element which belongs to a VB - VIII group, IB group, and an IIB group in the periodic table of a long period, and an oxide are

included as a principal component.

[0054] As a metallic element effective in a steam-reforming reaction, a partial oxidation reaction, or a decomposition reaction, it is desirable to use a VIII group's metal as an indispensable component. as a desirable metallic element, it is nickel, Rh, Ru, Ir, Pd, Pt, Co, and Fe among them, and independent in these -- or it combines and uses. It is desirable to add VB group's V, Nb, a VIB group's Cr, Mn and W, and a VIIB group's Mn, Re, etc. as a co-catalyst for these metal components. Moreover, it is good as a carbon deposit inhibitor to also add alkaline earth metal. These metals are usually supported on a heat-resistant oxide. While raising the specific surface area of a catalyst and raising activity by this, the endurance over high reaction temperature is made to give.

[0055] As a heat-resistant oxide, aluminum  $2O_3$ ,  $SiO_2$ ,  $TiO_2$ ,  $ZrO_2$  and  $MgO$  or a zeolite, SAPO, ALPO, stratified compounds, and these multiple oxides can be used. That the specific surface area of whose is usually  $5-300m^2/g$  is used for these heat-resistant oxides. These heat-resistant oxides and the above-mentioned metal component are compounded by well-known technique, such as the chemical technique, such as dip coating, a coprecipitation method, and a sol gel process, and physical mixing. Also usually let specific surface area of the catalyst after composition be the range of  $5-300m^2/g$ . When the specific surface area of a catalyst is under  $5m^2/g$ , activity falls and  $300m^2/g$  is exceeded, the property change under an elevated temperature becomes remarkable, and it is inferior to endurance. In addition, about the range of this specific surface area, it corresponds also to the catalyst at large mentioned later.

[0056] As a heat-resistant oxide, an alumina (aluminum  $2O_3$ ) is comparatively cheap, and in order to show a high specific surface area at the time of an elevated temperature, it can use preferably. Moreover, the multiple oxide of the spinel which made the alumina add a magnesia, and the magnesia singleness which is basic support in order to control a deposit of carbon or a magnesia can be used.

[0057] The rate of the catalyst metal added to a heat-resistant oxide has the desirable range of 1 - 30wt%. since activity is high in the case of the metal of a noble-metals system -- a maximum of 10 -- although it comes out enough even by addition of an about [ wt% ], in the case of metals of a base-metal system, such as nickel, it is desirable to consider as the range of 10 - 30wt%.

[0058] As a suitable catalyst for CO water gas shift reaction, although a VIII group's Fe, Co, IB group's Cu, an IIB group's Zn, etc. are often used, as for the metallic element specified by this application, the activity is shown not a little. The metal in which activity is shown at low temperature can secure thermal resistance by supporting these to heat-resistant oxides, such as the above-mentioned alumina, including Cu and Zn systems or both comparatively. As an addition to the heat-resistant oxide of the metal in this case, the range of 10 - 50wt% is desirable. In addition, when making it react at an elevated temperature comparatively, the spinel itself, such as Fe-Cr, can be used.

[0059] As a suitable catalyst for CO alternative oxidation reaction, metals, such as Co of a VII group's Mn and a VIII group, and Cu, Ag, Au of noble metals and IB group, can usually be supported and used for the above-mentioned heat-resistant oxide. It is possible to use Pt which does not need to oxidize to the generated hydrogen and has CO and a strong interaction. Moreover, a hopcalite catalyst can also be mentioned as one of the suitable examples.

[0060] Moreover, when carrying out covering support of these catalysts at the base of honeycomb structure, it is desirable to be referred to as 5-100 micrometers as thickness. When thickness is thinner than 5 micrometers, the fall of activity is brought about, and in being thicker than 100 micrometers, it brings about increase of a pressure loss.

[0061] Since a temperature fall is most caused the direction of a center where a reaction fluid flows more, and near [ where the concentration of a reaction fluid is high ] the entrance when a reaction is endothermic reaction, it is [ that the whole or a part should just generate heat ] desirable [ pyrexia and a catalyst object ] to use the structure which can carry out partial pyrexia of near pyrexia and the catalyst object a part for a core and near the entrance, as the term of the 1st and the 2nd invention described. A 30-1000 cc [ per piece ] thing is usually used for the volume of pyrexia and a catalyst object. the pyrexia and the catalyst per piece -- it is desirable that the exoergic section whole product in the living body carries out to to a maximum of 300 cc. it is because heat capacity becomes large and it has that great energy is necessity and heating area sufficient if it is 300 cc or less to heat the catalyst object by the side of back wash, when a whole product exceeds 300 cc.

[0062] As a cross-section configuration of pyrexia and a catalyst object, the configuration of arbitration, such as a round head of about 50-200mm, a rectangular head, and an ellipse, can usually be taken. Moreover, when using for a large-sized hydrogen generator, within a can, more than one can be attached and it can also use. Moreover, the hole configuration of a honeycomb structure object can take the configuration of arbitration, such as a round head, a rectangular head, a polygon, and corrugated one.

[0063] In addition, although the pyrexia and the catalyst object in the 3rd invention make the catalyst which generates hydrogen contain instead, it can regard an invention concept as the pyrexia and a catalyst object which made the catalyst which causes endothermic reaction contain. This is the 10th invention and other configurations are the same as that of

the 3rd invention.

[0064] Next, this application the 4th and 5th invention is explained using drawing 6 . In drawing 6 , 1st heater unit 10a, 1st catalyst object 11a, 2nd heater unit 10b, 2nd catalyst object 11b, 3rd heater unit 10c, and 3rd catalyst object 11c are arranged in the fluid passage (can) 12. The catalyst function of the reaction of either a steam-reforming reaction, a partial oxidation reaction and a decomposition reaction is given to 1st heater unit 10a and 1st catalyst object 11a, the catalyst function of CO water gas shift reaction is given to 2nd heater unit 10b and 2nd catalyst object 11b, and the catalyst function of CO alternative oxidation reaction is further given to 3rd heater unit 10c and 3rd catalyst object 11c. Moreover, power can be respectively supplied now to these heater units 10a, 10b, and 10c from an external power. the temperature sensing sensors (thermocouple) 14a, 14b, 14c, 14d, 14e, and 14f are arranged at the back-wash side of each heater units 10a, 10b, and 10c and catalyst objects 11a, 11b, and 11c. furthermore, if needed, a heat exchanger 17 is arranged in the back-wash side of 1st catalyst object 11a, and it is used for the preheating of a reaction fluid here.

[0065] In the 4th invention, energization is started first. a temperature predetermined [ as one operating method ] in the heater unit 10 -- it heats until 1st heater unit 10a reaches a temperature required for a steam-reforming reaction, a partial oxidation reaction, or a decomposition reaction still more preferably. 500 degrees C or more, a temperature required for a steam-reforming reaction, a partial oxidation reaction, or a decomposition reaction is 600 degrees C or more preferably, and carries out a temperature up by energization to this temperature. The method of controlling by the resistance welding time which could measure the temperature of the temperature of the 1st heater unit 10a itself, and was found beforehand is used. After carrying out a temperature up to this temperature, it is begun to pour a reaction fluid. Although it is desirable that the temperature of 500 degrees C or more preheats beforehand as for a reaction fluid, the steam-reforming reaction, partial oxidation reaction, or decomposition reaction on 1st heater unit 10a advances by what (continuation or intermittent energization) is energized to 1st heater unit 10a also at the temperature not more than it. by warming 1st catalyst object 11a by the side of back wash one by one with the reaction fluid which passed 1st heater unit 10a, and heating 1st catalyst object 11a, the energization to 1st heater unit 10a of the upstream can fall power, and a halt of energization of it is attained depending on the case.

[0066] By the same method, 2nd heater unit 10b is energized to 1st heater unit 10a and coincidence, and it waits for installation of a reaction fluid in the condition of having considered as 300 degrees C or more. It may be energizing in the meantime or energization may be stopped. 3rd heater unit 10c uses the same operating method as 2nd heater unit 10b except energizing to a condition 150 degrees C or more.

[0067] In this way, it is very possible to begin to generate hydrogen suitably between short time. The resistance welding time is for 60 seconds in general, and becomes possible [ pouring a reaction fluid by this time amount termination ].

[0068] Drawing 14 shows the reforming reactor concerning this application the 2nd invention, and consists of a reforming reactor with which catalyst object 20a of each 1st which has an exoergic function, 2nd catalyst object 20b, and 3rd catalyst object 20c were arranged. Therefore, the operating method is [ that the operating method concerning the 5th invention should just heat the catalyst objects 20a, 20b, and 20c instead of carrying out energization heating of the heater unit ] as unchanging as the 4th invention in any way. Then, all future explanation is explained as a catalyst object and a case where the heater unit was arranged according to the individual.

[0069] Still more nearly another operating method is explained in the reforming reactor shown in drawing 6 . That is, inactive gas or air etc. is circulated at the same time it starts the energization to the heater unit 10. In the case of a steam-reforming reaction catalyst, cautions are needed in order that the gas containing oxygen may oxidize a catalyst. heat transfer of the heat generated in the heater unit 10 is carried out by installation of inert gas to inert gas, and it heats the catalyst object 11 by the side of back wash further by it. It is begun at least to pour a reaction fluid in 1st heater unit 10a and the place where 1st catalyst object 11a reached operative temperature still more preferably. At this time, it is still more desirable the 2nd, the 3rd heater unit 10b and 10c, and that the 2nd and 3rd catalyst object 11b and 11c has reached operative temperature further. The standard of the resistance welding time is a maximum of about 120 seconds, a pre-heating property is very high as compared with the conventional technology, since the catalyst object 11 is heated further beforehand, labile is high, and there is a merit which can process comparatively many reaction fluids.

[0070] It is comparatively begun for example, after 10 seconds furthermore, for energization of the heater unit 10 to be started and to pour a reaction fluid to the inside of a short time as another operating method. the amount of the reaction fluid to pour is controlled and a reaction flow rate is resulted in the temperature rise of the catalyst object 11 by the side of back wash, or the heater unit 10 at increase and a steady state with the amount in which a reaction fully advances with the catalyst on 1st heater unit 10a preferably a sink and after that. Fully acting is possible even if it can carry out actuation initiation extremely for a short period of time, and it begins to pour a reaction fluid to coincidence mostly with energization by this method, when extreme. In addition, it is important to carry out preheating of the reaction fluid to at least 500 degrees C or more and 700 more degrees C or more in the phase in early stages of an inflow in this case.



[0071] Furthermore, it is made to arrive at the temperature region of the complete oxidation reaction of an organic compound, i.e., a temperature region 300 degrees C or more, and it is begun for energization of the heater unit 10 to be started, and to pour a reaction fluid as another operating method, at temperature with a temperature of 3rd heater unit 10c higher than alternative oxidation reaction of CO. Although some organic compounds reach 3rd heater unit 10c in the unreacted condition, while the 1st and 2nd heater units 10a and 10b and catalyst objects 11a and 11b do not fully act, it is discharged by combustion out of the system of reaction. After the 1st and 2nd heater units 10a and 10b and catalyst objects 11a and 11b fully begin to act, the output of 3rd heater unit 10c is fallen or stopped before that, and to the alternative reaction temperature region of CO, temperature is reduced and it operates regularly after that. It is possible to pour a reaction fluid further extremely also in this case for a short time at energization and coincidence. In addition, use as a source of heating of the fuel cell itself, or a heat exchanger is made to intervene, and the exhaust gas at the time of starting can also carry out heat recovery.

[0072] although the pre-heating nature of a reforming reactor is raised by using like the above a heater unit or the catalyst object in which energization pyrexia is possible and it is possible -- the above-mentioned method -- independence -- or you may combine and use it and the combination of a heater unit and the catalyst object which can be energized is also arbitrary.

[0073] Next, this application the 6th and 7th invention is explained using drawing 6 . Although the 4th invention is just going to indicate about an operating method until the catalyst object 11 carries out pre-heating, even after the catalyst object 11 arrives at a proper temperature region, in order to maintain a reaction suitably, the following operating methods are used. After 1st heater unit 10a and 1st catalyst object 11a arrive at the temperature region of a steam-reforming reaction, since it is usually endothermic reaction, in the case of a steam-reforming reaction, the reaction temperature of 1st heater unit 10a and 1st catalyst object 11a falls with inversion of a reaction. therefore, since a stable reaction is gone on, energization heating of the 1st heater unit 10a is carried out continuously or intermittently, and the temperature of the 1st catalyst object 11 by the side of 1st heater unit 10a and back wash is stabilized. About supply of power, you may be a fixed value and it may carry out adjustable according to the temperature of 1st heater unit 10a and 1st catalyst object 11a.

[0074] In order that 1st heater unit 10a and 1st catalyst object 11a may reduce fluid temperature by endothermic reaction also about the 2nd and 3rd heater units 10b and 10c, It energizes if needed and energization heating of the temperature of 2nd and 3rd heater unitb [ 10 ] and 10c and 2nd, and 3rd catalyst object 11b is carried out by the technique of carrying out energization heating of the 1st heater unit 10a, and the same technique. When the temperature of 1st heater unit 10a and 1st catalyst object 11a is stability with energization heating to 1st heater unit 10a, the energization to the 2nd and 3rd heater unit 10b and 10c is not necessarily required.

[0075] Moreover , even if it be desirable to use the structure where of the amount of core can carry out [ in the case of a heater unit ] the partial pyrexia of near the entrance in the case of the catalyst object which can generate heat by energization again since a temperature fall be most bring about near the entrance where the concentration of a direction of center where reaction fluid flow more when reaction be endothermic reaction , although [ the term of the 1st - the 3rd invention described ] and , and reaction fluid be high and it combine these partial pyrexia suitably further , it can use .

[0076] When 1st catalyst object 11a is a partial oxidation reaction Although there are not exothermic reaction, therefore implications positively heated in a steady state, since a reforming reactor may be cooled and a reaction may go up and down self-excited vibration periodically [ whenever / lifting catalyst temperature ] according to the vehicle speed also in the case of a stationary type, in for mount In order to make it react to stability more, it is desirable to make stability temperature of the heater unit 10 and the catalyst object 11 by energization.

[0077] In addition, any temperature of a heater unit, a catalyst object, and a reaction fluid is measured in the part of arbitration, processes the obtained data by computer, and can generate [ either of the above-mentioned operating methods, or ] hydrogen suitably combining these operating methods.

[0078] Next, the operating method at the time of mount is stated to details. When starting a vehicle, it is made to drive using a dc-battery first. It begins to energize with a dc-battery about the catalyst object which can generate heat by the heater unit or energization to coincidence. Furthermore, a reaction fluid, for example, a gasoline, and a methanol are made to evaporate with a dc-battery etc. similarly, and it introduces into a reforming reactor. Using the reforming reactor, heater unit, and/or catalyst object of this invention, it is begun suitably for pre-heating of the reforming reactor to be carried out, and to generate hydrogen by the operating method of this invention. In addition, the power supply of a capacitor (capacitor) etc. is also effectively utilizable for the pre-heating of a reforming reactor. Furthermore, after pre-heating of the reforming reactor is carried out, it is begun to turn an electric organ, and in order to enable stable operation of about [ utilizing for charge of a dc-battery the electrical energy obtained there ], and a reforming reactor, it lets direct or a transformer pass from an electric organ, and energizes on the catalyst object which can generate heat by



the heater unit or energization.

[0079] CO concentration after CO water gas shift reaction completion is about 10000 ppm, and CO is usually reduced to 10 ppm or less by CO alternative oxidation reaction. As an interesting application, the method which combined this invention and a hydrogen permeable film is also more desirable, and it is used that a steam-reforming reaction removes hydrogen out of the system of reaction, in order to act in favor of balance top hydrogen generating.

[0080] Moreover, it is also one of the desirable embodiments to install the heater unit explained by this invention in the upstream of this reforming reactor, and to use it for it at the preheating of a reaction fluid. When the heater unit which consists of a honeycomb structure object especially is used as a heater for preheatings of a reaction fluid (it is not necessary to cover a catalyst on a heater in this case), heat exchange effectiveness is large, and since there is the rectification effect of gas, it is more desirable.

[0081] As mentioned above, although the operating method of a reforming reactor was explained, most of these operating methods are applicable also to the operating method of the catalyst equipment which is this application the 11th and 12th invention.

[0082]

[Effect of the Invention] As explained above, according to this invention, the hydrogen for the fuel cells of a high grade can be generated as industrial use or an object for mount in a short time. Moreover, in the catalyst equipment which causes endothermic reaction, reaction temperature is suitably maintainable.

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[Translation done.]

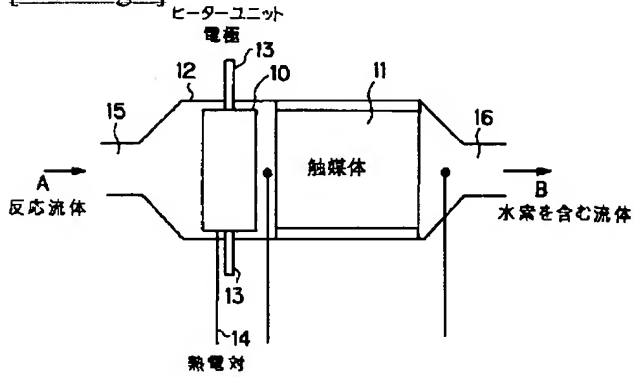
## \* NOTICES \*

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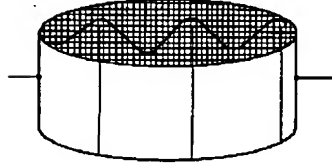
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

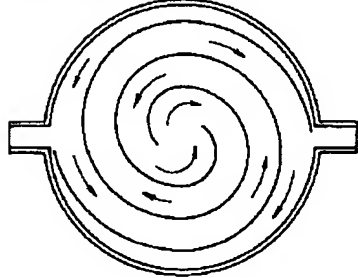
[Drawing 1]



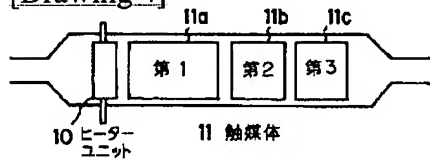
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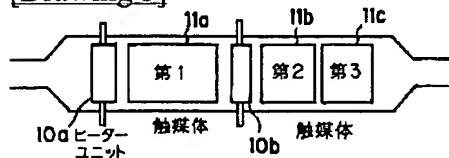
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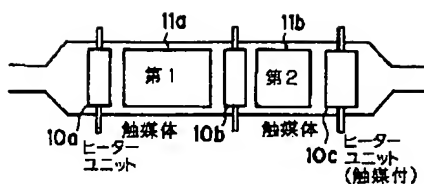
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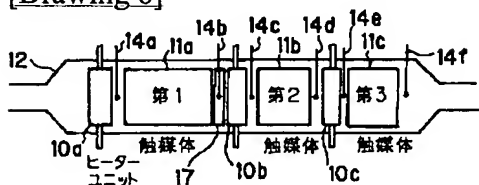
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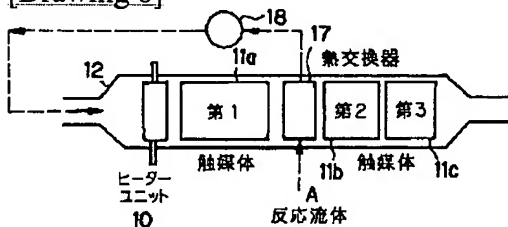
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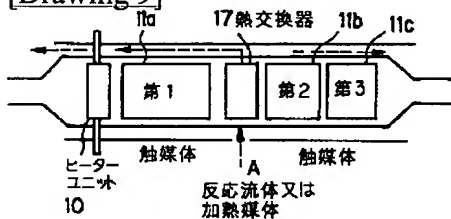
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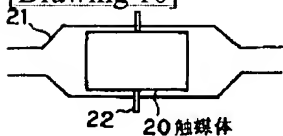
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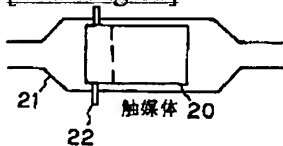
[Drawing 9]



[Drawing 10]

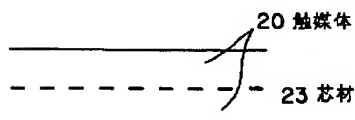


[Drawing 11]

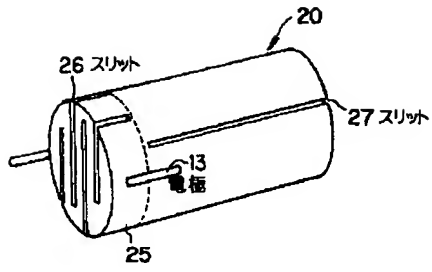


[Drawing 12]

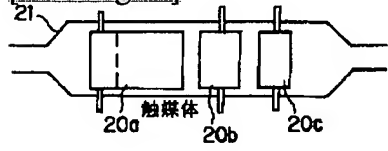
(第2の発明：メッシュワイヤの事例)



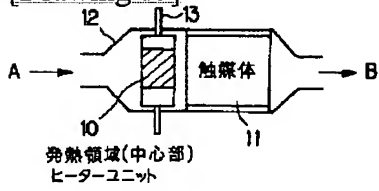
[Drawing 13]



[Drawing 14]



[Drawing 15]



[Translation done.]